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(54) TRACE ELEMENT FERTILIZERS

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to solid water-soluble trace element fertilizers.

For normal plant growth, it is necessary to feed the plant not only with the well-known main nutrients but also with magnesium and nutritious trace elements such as iron, manganese, copper, zinc, boron, cobalt and molybdenum. These trace element nutrients are necessary for building up enzyme systems in the plant cells. If only one of the said trace elements is withheld or is not fed at an adequate rate, signs of undernourishment occur. A well-known example is the chlorosis caused in plants due to a deficiency of iron. This may be cured by feeding the required iron ions in the form of a soluble iron compound to the sick plant either via its leaves or through its roots.

Particularly effective compounds for this purpose are the iron chelate complexes of N-carboxyalkylamino acids, e.g. ethylenediamino tetra-acetic acid. The metal complexes of other trace elements also have a better action than the simple inorganic salts (Stanley Chabarek and Arthur Martell, "Organic Sequestering Agents", John Wiley and Sons, Inc., 1959).

For these reasons, such metal chelates are used in agriculture for the cure or prevention of plant diseases resulting from trace element deficiency.

Such trace element fertilizers are commercially available in both solid and solution forms, although naturally preference is given to solid fertilizers, since these are cheaper to transport and store. These solid trace element fertilizers are mainly single- component fertilizers, only a comparatively small amount of said fertilizers being mixtures containing more than one trace element. This is probably due to the fact that the chelate complexes of the individual trace elements to be added to the mixture must be prepared in separate operations. Such multi-component systems are very expensive on account of their high manufacturing cost.

The present invention seeks to provide a solid trace element fertilizer which is simple to manufacture, has good storability, may be easily and quickly converted to a ready-to-use form by dissolution in water or spray liquids and fully satisfies all activity requirements.

According to the invention there is provided a solid water-soluble trace element fertilizer comprising magnesium and one or more of the trace elements iron, manganese, copper, zinc, cobalt and nickel, the magnesium and the iron (when present) being in sulfate, nitrate or chloride salt form or in the form of an N-carboxyl alkyl amino acid chelate compound and the manganese, copper, zinc, cobalt and nickel (when such elements are present) being in sulfate, nitrate or chloride salt form, and one or more N-carboxyalkamino acid sodium and/or potassium salts.

The solid water-soluble trace element fertilizers of the invention may be manufactured by simply mixing the components, and it is no longer necessary to manufacture the individual chelate complexes in separate operations. Surprisingly, they are stable on storage and show virtually no change when stored for relatively long periods, although they contain components which could react with each other, at least in the presence of moisture. As a basic rule, all sulphates, nitrates and chlorides of the known trace elements iron, manganese, copper, zinc, cobalt and nickel may be used. These compounds may be mixed in any desired proportions, depending on the use to which the trace element fertilizer is to be put. Usually, the salts of iron and magnesium constitute a major portion of the trace element fertilizer, and it is advantageous, from the storage stability point of view, to use only those chlorides, sulphates and nitrates of said elements which contain not more than 6 molecules of water of crystallization per atom of metal. Examples of such salts are not only the simple salts containing water of hydration but also the double salts, e.g.

$MgNH_4Cl_3.6H_2O$, $MgK_2(SO_4)_2.6H_2O$,
$MgNa_2(SO_4)_2.4H_2O$,
$Mg(NH_4)_2(SO_4)_2.6H_2O$,
$Fe(NH_4)_2(SO_4)_2.6H_2O$.

It is preferred to use the trace elements in their divalent form.

In addition to the aforementioned trace elements, the trace element fertilizers may of course also contain other trace elements such as boron in the form of boric acid and its water-soluble salts (the term boric acid including its anhydride), or molybdenum in the form of water-soluble molybdates.

Particularly suitable sodium and/or potassium salts of N-carboxyl-alkylamino acids are the salts of nitrilo triacetic acid (NTA), ethylenediamino tetra-acetic acid (EDTA), diethylenetriamino penta-acetic acid (DTPA), hydroxyethylethylenediamino triacetic acid (HEEDTA) and cyclohexane-1,2-diamino tetraacetic acid (CDTA). For convenience, these compounds are referred to below by the abbreviations given above in brackets.

It is not necessary to use the said acids exclusively in the form of their sodium and/or potassium salts; they may be partially replaced by the corresponding free acids. The addition of said free acids makes it possible to adjust the pH of the aqueous solutions prepared from said solid trace element fertilizers to any value, from about 4 to 7.5.

The amount of sodium and/or potassium salts of N-carboxylalkylamino acids, or the amount of such salts and free acids combined, will in general be such that at least 20% and preferably at least 40% of the divalent and trivalent metal ions present in the mixture may be complexed. An excess of said acids or their salts of, say, up to 100% is not detrimental, since this will serve to remobilize any trace elements which have become anchored in the soil.

It will be appreciated that water-soluble compounds of macronutrient elements may also be added to the trace element fertilizers of the invention.

Example.

Solid water-soluble trace element fertilizers are made by finely milling the compounds listed in the Table below in a cross-beater mill to give a homogeneous mixture thereof.

The resulting mixtures are found to be stable on storage over relatively long periods, i.e. they do not show changes sufficiently acute to impair handling thereof. They remain free-flowing even when stored at elevated temperatures. In a stability test carried out over 24 hours at 40°C, no caking of the mixture was found to take place, not even in the case of mixtures 5 and 7 containing epsom salts ($MgSO_4.7H_2O$), although the partial vapour pressure of water above these salts at this temperature is considerable and although epsom salts decompose at 48°C with the elimination of water.

The said trace element fertilizers may readily be dissolved to give concentrated solutions. Their rate of dissolution is excellent. For example, 100 g of the mixtures listed in the Table below dissolve in 400 c.c. of water at temperatures of from 23° to 25°C within about 3 minutes with stirring. Only significant residues of undissolved portions of less than 0.3% by weight remains.

TABLE

Parts by weight

Ingredients		Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7
Fe	$(NH_4)_2Fe(SO_4)_2.6H_2O$	16.0	—	—	—	—	14.0	—
	$FeCl_3$	—	—	7.3	—	18.9	—	—
	Fe-EDTA (5% Fe)	—	40.3	—	25	—	—	—
	$FeSO_4.7H_2O$	—	—	—	—	—	—	6.8
Mn	$MnSO_4.1H_2O$	6.7	5.9	7.2	4.8	3.6	7.5	4.1
B	H_3BO_3	9.1	8.0	9.9	4.3	3.3	—	5.5
Cu	$CuSO_4.5H_2O$	3.4	3.0	3.6	1.8	1.4	2.9	2.0
Zn	$ZnSO_4.7H_2O$	3.2	2.8	3.4	2.1	1.5	3.2	2.0
Co	$CoCl_2.6H_2O$	0.2	0.2	0.2	0.1	0.1	0.2	—
Ni	$Ni(NO_3)_2.6H_2O$	0.7	0.6	0.7	—	—	—	—
Mo	$(NH_4)_6Mo_7O_{24}.4H_2O$	0.09	0.08	0.09	0.05	0.04	0.08	0.05
MgO	$MgSO_4.2,4H_2O$	20.5	18.1	22.2	—	—	23	—
	$MgSO_4$	—	—	—	9.4	—	—	—
	$MgSO_4.7H_2O$	—	—	—	—	14.4	—	18.8
	Na_3-NTA	—	—	—	—	7.3	—	—
	NA_4-EDTA (85%ig)	37.1	20.8	45.2	48.2	87.7	—	52.7
	Na_5-DTPA	—	—	—	—	—	40	—
	NTA	—			—	—	—	

TABLE—Continued

Ingredients	Parts by weight Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7
EDTA	—			3.2	7.4	—	
DTPA	—			—	—	4.3	
HEEDTA	3			—	1.5	—	
CDTA	—			1.0	—	—	
Percentage of chelated di- und tri-valent metal ions	40	40	40	100	150	40	80

WHAT WE CLAIM IS:—

1. A solid water-soluble trace element fertilizer comprising magnesium and one or more of the trace elements iron, manganese, copper, zinc, cobalt and nickel, the magnesium and the iron (when present) being in sulfate, nitrate or chloride salt form or in the form of an N-carboxyalkyl amino acid chelate compound and the manganese, copper, zinc, cobalt and nickel (when such elements are present) being in sulfate, nitrate or chloride salt form, and one or more N-carboxyalkylamino acid sodium and/or potassium salts.

2. A trace element fertilizer as claimed in claim 1 additionally containing boric acid and/or a water-soluble salt thereof.

3. A trace element fertilizer as claimed in claim 1 or 2 additionally containing a water-soluble molybdate.

4. A trace element fertilizer as claimed in any of claims 1 to 3 containing, as trace elements, iron, manganese, copper, zinc, cobalt and nickel.

5. A trace element fertilizer as claimed in any of claims 1 to 4, containing iron and magnesium in the form of sulphates, nitrates and/or chlorides containing not more than 6 molecules of water of crystallization per atom of metal.

6. A trace element fertilizer as claimed in any of claims 1 to 5, wherein iron and magnesium are present, at least in part, in the form of chelate compounds with an N-carboxyalkylamino acid.

8. A trace element fertilizer as claimed in any of claims 1 to 7, wherein the free N-carboxyalkylamino acid(s) (if present) is, or the acid from which the sodium and/or potassium salt is derived is, nitrilo triacetic acid, ethylenediamino tetraacetic acid, diethylenetriamino pentaacetic acid, hydroxyethylethylenediamino triacetic acid or cyclohexane-1,2-diamino tetraacetic acid.

9. A trace element fertilizer as claimed in any of claims 1 to 8 containing one or more sodium and/or potassium salts of N-carboxy-

alkylamino acids with or without free N-carboxylalkylamino acid in a total amount sufficient to complex at least 40% of the divalent and trivalent metal ions present in the mixture.

10. A trace element fertilizer as claimed in claim 1 and substantially as hereinbefore described and exemplified.

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